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14. ABSTRACT Ensuring fuel suitability is a challenge faced by aerospace propulsion development programs. Specifically, reliable and predictable thermal management of engine and vehicle structures, and more precisely the fuel's ability to absorb heat without detrimentally affecting cooling system performance and reliability, is a common requirement for aircraft, rockets, and hypersonic vehicles. The Aerospace Fuels Quality Test and Model Development (AFQTMoDev) project was initiated to mature fuel quality assurance practices for rocket grade kerosene, thereby ensuring operational readiness of conventional and alternative fuels. During the first two years of the effort, a compact, relevant thermal integrity test metrology was developed, applied to a compositionally diverse set of fuels, and evaluated on the merits of repeatability, sensitivity, and characteristics amenable to standardization. Furthermore, in an attempt to explain the influence of physical and chemical variables on the complex deposit formation process, chemometric approaches [principal component analysis (PCA), tile-based Fisher Ratio (F-ratio) analysis, and partial least squares (PLS) analysis] were applied to multivariate datasets comprising comprehensive chromatographic data (GCxGC – TOFMS) and quantitative fuel thermal integrity data, resulting in predictive models correlating fuel composition with observed behavior. Together, these accomplishments demonstrate advancements in both fit-for-purpose fuel thermal performance evaluation for quality assurance and the application of advanced analytical tools to a complex physicochemical process.				
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Hydrocarbon Fuel Thermal Performance Modeling based on Systematic Measurement and Comprehensive Chromatographic Analysis

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Ensuring fuel suitability is a challenge faced by aerospace propulsion development programs. Specifically, reliable and predictable thermal management of engine and vehicle structures, and more precisely the fuel's ability to absorb heat without detrimentally affecting cooling system performance and reliability, is a common requirement for aircraft, rockets, and hypersonic vehicles. The Aerospace Fuels Quality Test and Model Development (AFQTMoDev) project was initiated to mature fuel quality assurance practices for rocket grade kerosene, thereby ensuring operational readiness of conventional and alternative fuels. During the first two years of the effort, a compact, relevant thermal integrity test metrology was developed, applied to a compositionally diverse set of fuels, and evaluated on the merits of repeatability, sensitivity, and characteristics amenable to standardization. Furthermore, in an attempt to explain the influence of physical and chemical variables on the complex deposit formation process, chemometric approaches [principal component analysis (PCA), tile-based Fisher Ratio (F-ratio) analysis, and partial least squares (PLS) analysis] were applied to multivariate datasets comprising comprehensive chromatographic data (GC×GC – TOFMS) and quantitative fuel thermal integrity data, resulting in predictive models correlating fuel composition with observed behavior. Together, these accomplishments demonstrate advancements in both fit-for-purpose fuel thermal performance evaluation for quality assurance and the application of advanced analytical tools to a complex physicochemical process.

I. Introduction

In hydrocarbon-fueled liquid rocket engines, combustion enthalpy is transferred at high rates to thrust chamber surfaces, which are maintained at acceptably low temperatures by a regenerative cooling system. Typical chemical and physical conditions are indicated for a notional regenerative cooling channel in Fig. 1. Table 1 compares cooling system environments of several aerospace applications. Ensuring reliable and predictable fuel thermal performance and material compatibility is crucial, particularly as operating regimes and fuel composition extend beyond the domestic experience base. Full scale component or engine testing can assess a candidate fuel's suitability but may be prohibitive due to schedule and cost. Instead, reliable methods by which to systematically evaluate and predict thermal performance of candidate fuels under relevant conditions are desired.

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Aerospace fuels, including rocket grade kerosene RP-1 and RP-2, are produced to meet physical property and

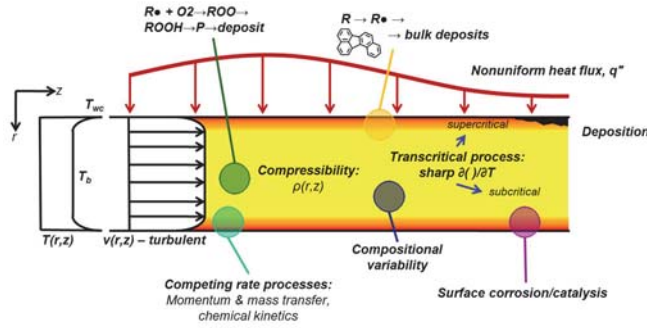


Figure 1. Rocket regenerative cooling channel environment and processes. r – radial direction; z – axial direction; v – fluid velocity; T_{wc} – wall temperature; T_b – fuel bulk temperature; q'' – heat flux; p – fluid density.

chemical composition specification requirements derived from considerations such as engine performance (combustion, cooling, material compatibility, etc.), safety, and cost and availability (see Table 2). Therefore, product quality is guaranteed only insofar as specification requirements and methods by which to assess them are relevant to the intended application. Although limitations on certain impurities (e.g., sulfur) are in place, controls on hydrocarbon type [e.g., straight chain (n-), branched (iso-), and cyclic paraffins] and distribution are not. Chromatograms demonstrating RP compositional variability are shown in Fig. 2 alongside aviation fuel. The premise for the Aerospace Fuels Quality Test and Model Development (AFQTMoDev)

project is that cooling system performance and reliability may be negatively impacted by compositional variation even for fuels meeting existing specification limits. Testing this assertion requires accounting for all potential compositional variations and quantifying their influence on cooling characteristics.

Table 1. Aerospace Cooling System Conditions and Environments

Application	T_{wc} (°F)	T_b (°F)	P (psi)	q'' (Btu/in ² s)	Primary Material
Rockets	500-900	100-500	700-7000	10-120	Cu alloys
Hypersonics	1200-1500	100-1300	500-1000	0.5-2	Ni alloys
Aircraft	300-400	100-300	500-800	<1	SS alloys

Table 2. Specification Limits for Aerospace Fuels

	ASTM Method	JP-5	Jet A	RP-1	RP-2
Specification		MIL-DTL-5624U	ASTM D1655-15	MIL-DTL-25576E	MIL-DTL-25576E
Requirement, Units					
Distillation, °C					
IBP	D86	report		report	report
10% recovered		<205	<205	(185-210) ^a	(185-210)
20% recovered		report			
50% recovered		report	report	report	report
90% recovered		report	report	report	report
End point		<300	<300	(<274)	(<274)
Density/15°C, kg/L	D1298	0.788-0.845	0.775-0.840	0.799-0.815	0.799-0.815
Viscosity/-20°C, mm ² /s	D445	<8.5	<8.0	<16.5 ^b	<16.5 ^b
Flash Point, °C	D93 ^c	>60	>38	(>60)	(>60)
Freezing Point, °C	D2386 ^d	<-46	<-40 ^e	(<-51)	(<-51)
Net Heat of Combustion, MJ/kg	varies ^f	>42.6	>42.8	(>43.0)	(>43.0)
Hydrogen, mass %	varies ^g	>13.4	>13.4 ^h	>13.8	>13.8
Aromatics, vol %	D1319	<25.0	<25.0	<5	<5
Olefins, vol %	D1319			<2.0	<1.0
Total sulfur, mass%	varies ⁱ	<0.3	<0.3	<0.003	<0.00001
Mercaptan sulfur, mass%	D3227	<0.002 ^j	<0.003 ^j	<0.0003	
JFTOT ΔP change, mmHg	D3241 ^k	<25	<25		report

Notes:

- ^a Parentheses denote unit conversion from detail specification.
- ^b Maximum value at -30°F (-34°C) is given.
- ^c D56 is preferred method for Jet A.
- ^d JP-5 also allows D5972; Jet A also allows D5972, D7153, and D7154.
- ^e Jet A-1 value: -47°C
- ^f JP-5, Jet A: D4809, D3338, or D4529; RP-1/RP-2: D240
- ^g JP-5: D3701; JP-8: D3701, D3343, or D7171; RP-1/RP-2: D3343
- ^h Value provided is for JP-8 (MIL-DTL-83133H).
- ⁱ JP-5: D1266, D2622, D3120, D4294, or D5453; Jet A: D1266, D2622, D4294, or D5453; RP-1: D5453 or D5623; RP-2: D4045 or D5623
- ^j Alternatively, D4952 can be used with sweet/negative result.
- ^k JP-5, Jet A: 260°C for 150 min.; RP-2: 355°C for 300 min.

In addition to the apparent absence of adequate compositional limits, rocket kerosene is not quality tested for thermal stability or material compatibility prior to delivery and use in current launch vehicles. Specifically, RP-1 is not tested and RP-2 is tested using ASTM D3241 [“Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)”]^{Error!}

Reference source not found, but results are

reported, not constrained. In contrast, various test methods have been used in the past to evaluate and screen candidate aviation turbine fuels in a standardized way.² The suitability of D3241 for screening jet fuel based on thermal oxidative stability is not disputed in the current project. However, data suggests that this metrology is inadequate for ensuring rocket fuel quality for two primary reasons: (1) it does not prescribe materials or operating conditions present in rocket systems; and (2) it is incapable of clearly resolving performance differences for rocket fuels. Table 3 shows JFTOT results for several fuels, including the RP fuels shown in Fig. 2, along with JP-8. In a 5-hour test at a temperature of ~620°F (325°C), all RP fuels exhibited a visual tube deposit rating (TDR, a qualitative description of the deposit as compared with a standard color scale) of < 2; negligible differences in pressure differential were measured. Clearly, the JFTOT procedure as specified in MIL-DTL-25576E is unable to adequately discriminate between thermally stable rocket fuels that have been shown in higher fidelity testing to perform differently (for example, see Reference 3). The continued push toward more demanding cooling environments, coupled with the reality of fuel compositional variation within the specification limits, provides impetus for a devoted fuel thermal quality test.

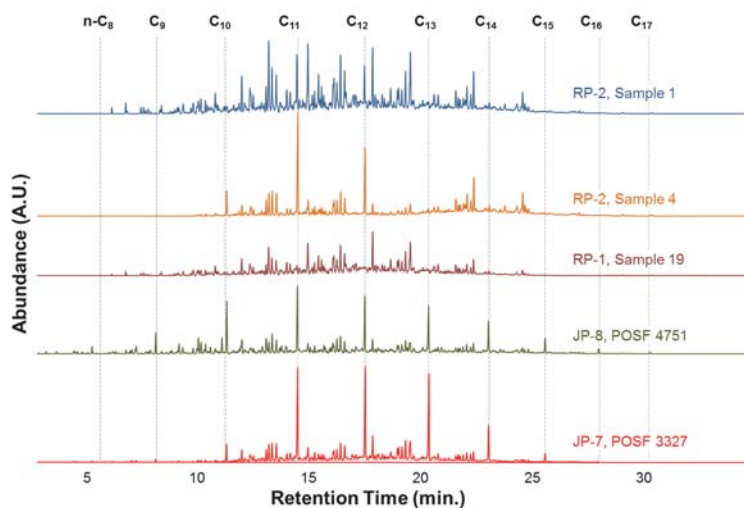


Figure 2. Chromatographic comparison of several aerospace fuels

Table 3. Results of ASTM D3241 Testing

Conditions: RP-1 (Sample 18): 355°C, 5 hr. All others: 325°C, 5 hr.

Fuel Type	JP-7	JP-8	RP-1	RP-2	RP-2	RP-1	RP-2	RP-1
POSF/Sample	3327/15	4751	19	4	1	14	6	18
Tube Deposit Rating Code	< 2	> 4A ^a	< 2	< 2	< 2	< 2	< 2	-
Maximum ΔP, mmHg	0.1	280.1	0.1	0	0.1	0	0	0

^a “A” denotes abnormal deposit; “P” denotes peacock deposit.

II. Approach

A. Project Structure

Given these technological challenges and existing shortcomings, objectives for the AFQTMoDev project are: (1) Demonstrate a fuel thermal integrity test metrology applicable to rocket cooling systems and capable of rapidly quantifying fuel quality using small volumes. (2) Develop and implement chemometric solutions for the purpose of correlating fuel chemical composition with physical performance. The technical effort was structured to achieve simultaneous progress in fundamental fuels understanding and product quality assurance methods: quantifying the impact of fuel chemistry on thermal performance improves specification and selection activities, while the experimental method itself is evaluated regarding its merit as a specification quality test. Additionally, a primary technical challenge was the integration of performance behavior and comprehensive chemical composition data (GC×GC – TOFMS), yielding quantitative and informative models and correlations. This required a highly collaborative and interdependent technical framework, which is depicted schematically in Fig. 3.

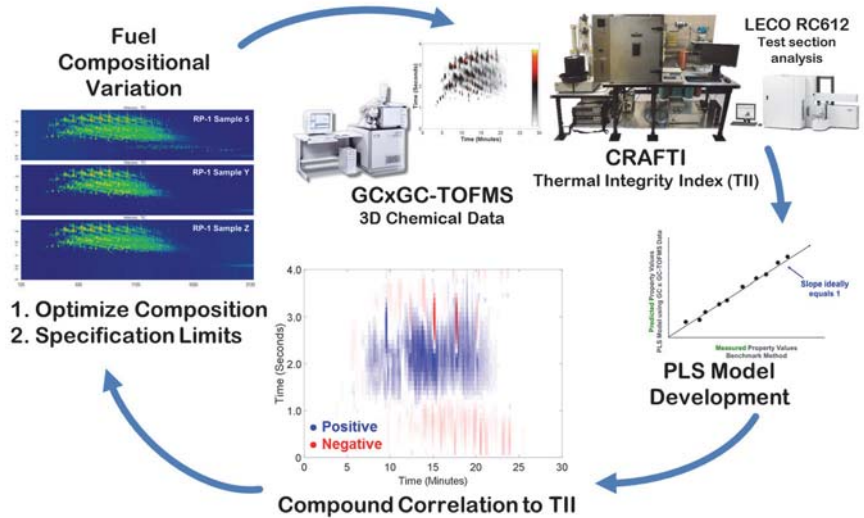


Figure 3. AFQTMoDev project structure

B. Experimental Methods

Recently, an experimental apparatus was designed and constructed for the purpose of evaluating the effects of fuel purification technologies on thermal stability and material compatibility. This compact rapid assessment of fuel thermal integrity (CRAFTI) was modified and extensively characterized under the AFQTMoDev project. In this versatile convective heat transfer experiment, fuel is pressurized by a positive displacement dual syringe pump and flows through an ohmically heated test article. Electrical current is maintained via algorithm control of the dual power supplies, resulting in constant power during the test. Backpressure is held constant by an electropneumatically controlled dome loaded backpressure regulator. Downstream heat exchangers in series cool the fuel to safe levels prior to sampling and collection. The experiment is conducted in vacuum to reduce heat loss to surroundings, minimize oxidation of test article surfaces, and isolate the operator from potential hazards. Figures 4 and 5 show the experiment and test article details, respectively. Combined control of fuel flowrate, test article geometry, and supply power defines surface temperature profile, which in turn determines fuel exit bulk temperature.

Recorded data includes flow rate, power supply current and voltage, fuel inlet and exit bulk temperature,

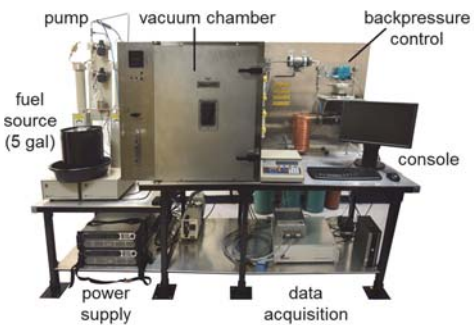


Figure 4. CRAFTI experimental apparatus

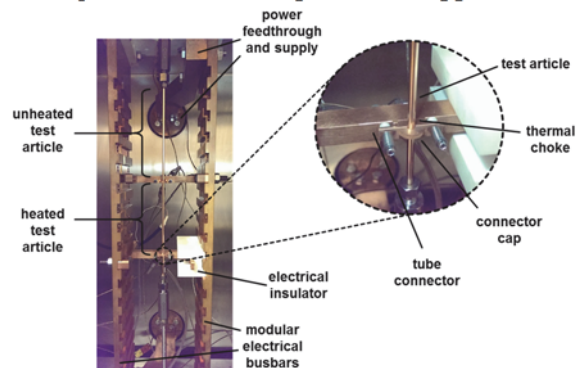


Figure 5. CRAFTI test article assembly showing connection details

fuel pressure, and test article outer surface temperature, measured at 0.5-in. (~ 1.3 cm) increments. In the existing apparatus, test article length can be varied from 2 – 16 in.; inner diameters (ID) ranging from 0.014 – 0.036 in. (0.36 – 0.91 mm) are available. For results reported herein, oxygen-free electrolytic (OFE) copper (C10100) test articles with 0.125-in. (3.2- mm) outer diameter (OD) and 4-in. (10-cm) heated length were used; other materials are readily accommodated as desired. Table 4 shows the parameters used for the results reported hereafter; these standard test conditions were selected based on the following criteria: (1) similarity to relevant cooling system environments; (2) ability to effect measurable differences in carbon deposit and pressure drop increase during a single test; and (3) order of magnitude reduction in fuel quantity required per test (50 gal baseline).

Nineteen fuels were evaluated, comprising eight (8) RP-2 samples, seven (7) RP-1 samples, JP-7, and JP-900. Extensive physical and chemical property data was acquired but is not included here; as an indication of sample variability, Figure 6 presents ASTM D86 distillation data for the nineteen fuels along with JP-8 and a historical RP-1 sample. Several of these fuels have been the subject of previous efforts.⁴⁻⁶

C. Analytical Methods

Test articles were used for a single test then sectioned, cleaned, and evaluated with temperature programmed oxidation

(TPO) using a multiphase carbon analyzer (RC612, LECO Corp.). As shown in Fig. 7, each test article was sectioned into twenty-two 0.5-in. long sections comprising inlet, heated, and exit regions. In order to differentiate between carbon allotropes present on test article surfaces, the following oxidation temperature program was used: 200s at 275°C (chemisorbed carbon and contamination introduced during test article handling); ramp to 400°C at 100°C/min and hold for 120s (amorphous carbon); ramp to 600°C at 100°C/min and hold for 120s (filamentous carbon); ramp to 900°C at 100°C/min and hold for 60s (crystalline carbon, usually in the form of graphite platelets, oxidizes at this high temperature). Due to thermal response and instrument control, actual analysis times differed from this control scheme; results hereafter are reported based on measured, not programmed, temperature time profiles. For each test, this

Table 4. Standard Test Conditions

Parameter	Value	Units
Reynolds Number, Re	2000-20,000	-
Test article material	Cu (C10100)	-
Input power	4500	W
Wall temperature (dependent variable)	~1050±250 (560±120)	°F (°C)
Backpressure	1,000 (6.9)	psi (MPa)
Heated length	4 (10.2)	in. (cm)
Test duration	15	min.

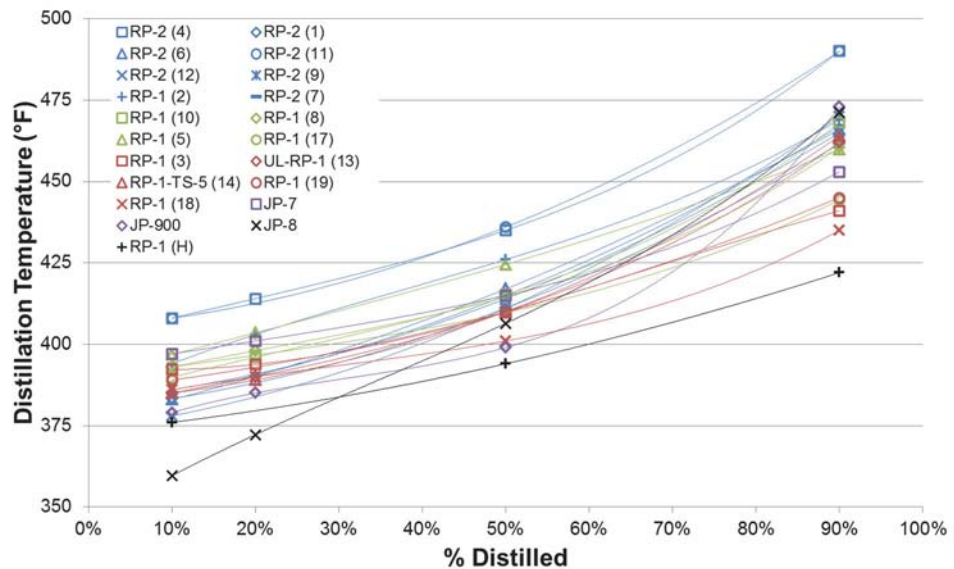


Figure 6. Referee fuel set ASTM D86 distillation. Colors indicate category: blue – recent formulations; green – existing lab blends; red – historical/reference fuels; purple – other markets.

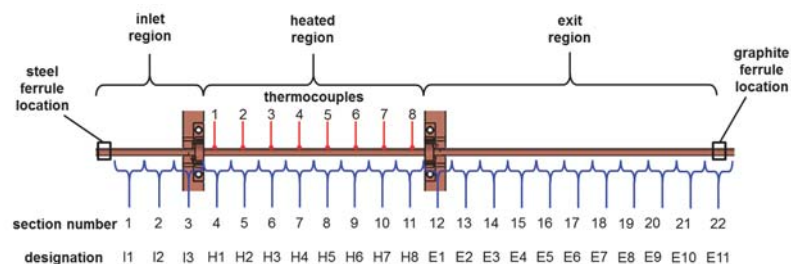


Figure 7. Test article heat transfer regions and analytical designations

method yields spatially-resolved carbon deposit as a function of analysis temperature, thereby providing simultaneous indication of the form and location of carbon deposit in the test article. In conjunction with CRAFTI physical data and chromatographic fuel compositional data, multivariate data amenable to chemometric analysis and model development is acquired.

Comprehensive fuel analysis was performed using GC×GC – TOFMS with a reverse column configuration to enhance separation and optimize selectivity for the nineteen fuel samples evaluated. In this configuration, the first dimension column (Rxi-17 Sil MS; 30m length, 250 μ m ID, 0.25 μ m film thickness) has a polar stationary phase and the second dimension column (Rxi-1 MS; 2m length, 180 μ m ID, 0.18 μ m film thickness) has a non-polar stationary phase. The modulation period was 4s. GC×GC – TOFMS resulted in a dataset with the following dimensions: 19 fuel samples \times 514 first dimension separation data points (i.e., 514 modulations at 4s each) \times 400 second dimension separation data points (i.e., 4s at 100 spectra/s) \times 300 mass channels (m/z) per spectrum.

D. Chemometric Data Analysis and Modeling

Although multidimensional chromatography has experienced increased applicability for aerospace fuel analysis, the extent of its utility has heretofore been limited in most cases to qualitative, often visual, comparisons between fuels and in some cases hydrocarbon type classification, owing to the immensity of the datasets offered by GC×GC. With the amount of chemical information obtained from GC×GC – TOFMS, there are significant challenges in glean useful information from the data. This project builds on recent successful efforts in the prediction of chemical and physical behavior using only GC×GC – TOFMS chromatographic data.^{7,8} Similar chemometric methods were implemented in the current work, but pursuant to a more formidable challenge: the prediction of complex, application-specific physicochemical behavior encountered in a regenerative cooling environment.

CRAFTI thermal integrity data, test article carbon deposit data, and comprehensive fuel chemical information, obtained with GC×GC – TOFMS, all obtained for a set of referee fuels, were analyzed using a variety of chemometric approaches. Principal component analysis (PCA) mathematically reduced the large multiparametric datasets in order to glean useful information about the fuels. PCA served two primary purposes: (1) Establish groups to distinguish between fuels with observed thermal integrity performance differences, thus serving the purpose of assigning categorical quality, i.e., high performing and low performing, for subsequent Fisher ratio (F-ratio) analysis; and (2) Identify GC×GC – TOFMS chromatographic variations, e.g., hydrocarbon compositional differences between fuels, that correlate with measured performance differences. F-ratio analysis also served dual purposes: (1) Produce a refined set of GC×GC-TOFMS data for the purpose of optimizing subsequent partial least squares (PLS) analyses; (2) Identify class distinguishing features, i.e., chemical compounds in the chromatographic data, that contribute to a fuel's group assignment, in this case thermal integrity. Finally, PLS was used to develop models that relate thermal integrity behavior to fuel composition. Predictive models were developed for physical behavior measured during CRAFTI testing (pressure drop) as well as for test article deposit formation measured during post-test analyses. One important outcome of PLS modeling is the ability to isolate and identify compounds and regions of chromatographic space that are responsible for an observed directional (positive or negative) change in a measured parameter.

III. Results

A. Test Method Repeatability

A viable thermal stability test method must yield empirical results that are: (1) consistent for a given fuel evaluated repeatedly at nominal operating conditions; and (2) of sufficient fidelity to distinguish composition-dependent behavior from behavior due to other influences. That is, the test metrology must be repeatable and sensitive. For inherently thermally stable fuel such as rocket grade kerosene, these criteria are exceedingly challenging due to low signal levels accompanying conventional measurement techniques (cf. Table 3) and the narrow allowable concentration range of compounds expected to adversely affect thermal performance (cf. Table 2). To demonstrate overall CRAFTI repeatability, a series of ten runs was conducted using RP-2 fuel (Sample 1) at the standard test conditions (Table 4) over a period of approximately one year. These runs were interspersed among nearly fifty others, many of which employed relatively high sulfur and aromatic content fuels. Only a simple purge/flush protocol was used between tests; no disassembly or special cleaning of wetted components was performed.

Figure 8 shows pressure drop time history for seven of the ten replicate runs. Reduction in cross-sectional flow area accompanying deposition of solid material can lead to pressure drop increase, although the initial increase in pressure drop in Fig. 8 (0-250s) is attributed to thermal equilibration of the fuel and experimental components. Pressure drop as a function of time shows similar transient response for the repeat tests: slope and inflection behavior is repeatable. Considering environmental differences and variations in test article cutting, end facing, and installation,

pressure drop repeatability is quite acceptable. As indicated, based on the inlet and outlet pressure transducers used in the apparatus (0.1% accurate), results for these seven tests are statistically indistinguishable.

Likewise, carbon deposit characteristics from TPO of test article surfaces indicates similar behavior for the ten replicate runs performed with RP-2 Sample 1, as seen in Fig. 9. The data represent mass of carbon deposited on the fuel-wetted (inner) surface of 0.5-in. (12.7-mm) long test article sections. Overall repeatability, which accounts for end-to-end variations in the CRAFTI experiment and post-test analysis, is encouraging considering that carbon levels are near the signal threshold. Furthermore, the ability of the CRAFTI metrology to reproduce carbon deposit behavior after a full year of testing with a variety of special blends, treated fuels, and worst case formulations, without full disassembly or extensive cleaning, indicates its excellent potential as an eventual test method.

B. Test Method Sensitivity

Although repeatable results for a given fuel indicate adequate experimental control and measurement protocol, the efficacy of the CRAFTI experiment to discriminate fuels based on thermal integrity related to chemical composition is requisite for its eventual consideration as a standard test method. Table 5 summarizes the conditions and results obtained for the nineteen referee fuels; entries are sorted based on pressure drop (ΔP) increase during the test. These results demonstrate two important characteristics of the CRAFTI metrology: (1) The method produces a thermal environment resulting in cooling channel fouling and concomitant ΔP increase even for short test durations (15 min.); and (2) This primary measurand (ΔP) is sufficiently resolved between fuels with relatively slight compositional differences. It is noteworthy that the fuels indicated by shaded rows in Table 5 exhibited no discernable ΔP differences when evaluated using ASTM D3241 (cf. Table 3). Evaluated with CRAFTI, the same fuels demonstrate ΔP increase of between 40-630% of the initial value. Perhaps even more remarkable is that most of the fuels evaluated met the current specification (all fuels met the specification in place at the time of their production).

Additional evidence for the viability of the CRAFTI method with respect to repeatability and sensitivity is provided in Fig. 10, which shows time-averaged surface temperature as a function of measurement position for five individual runs of two compositionally unique fuels. These fuels possess different temperature profile behavior compared with one another, yet exhibit reasonable repeatability when evaluated multiple times at the standard test conditions. The causes of these unique temperature profiles are not immediately clear; however, a variety of experimental conditions are expected to contribute (e.g., property gradients and transcritical flow, effects of deposit formation on local heat transfer, etc.), the influences of which are currently being characterized in parallel computational fluid dynamics (CFD) simulations.⁹

To further illustrate and emphasize the sensitivity of the CRAFTI method and analytical protocol, TPO analysis time-integrated (total) carbon data averaged for multiple replicate runs is presented for five representative fuels as a

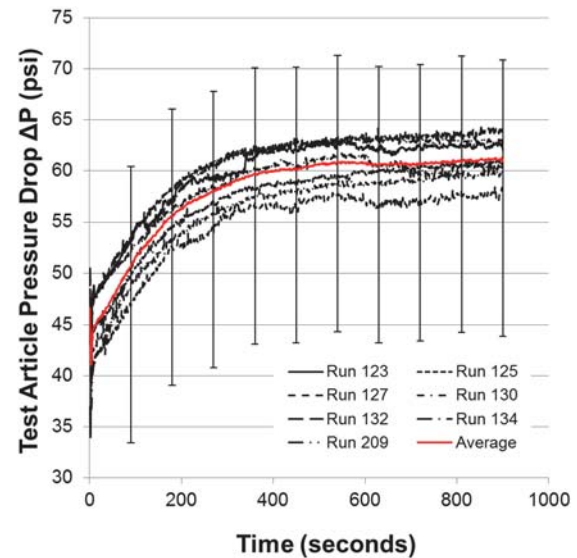


Figure 8. Pressure drop repeatability

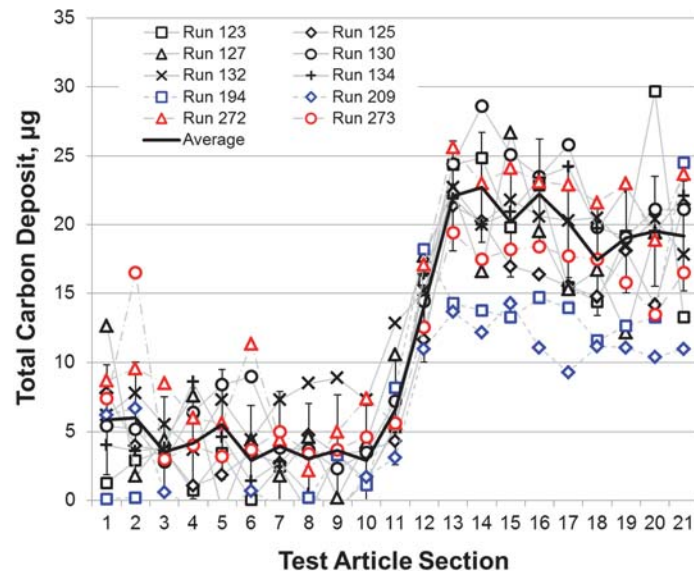


Figure 9. Carbon deposit formation repeatability

Table 5. Summary of CRAFTI Evaluation of Referee Fuel Set

Fuel	Sample	# of Runs	Avg. T_{wall} [$^{\circ}$ F ($^{\circ}$ C)]	$\Delta P_{initial}$ [psi (kPa)]	ΔP Increase [psi (kPa)]
RP-2	1	10	1158 (626)	44 (306)	16 (113)
RP-2	4	4	1026 (552)	42 (288)	20 (136)
RP-2	7	2	1048 (564)	39 (269)	21 (142)
RP-1	3	7	1112 (600)	46 (320)	21 (146)
UL-RP-1	13	2	1115 (602)	33 (225)	22 (154)
RP-2	9	4	1110 (599)	31 (213)	23 (158)
RP-2	6	2	1145 (618)	47 (326)	23 (158)
RP-1	10	2	1057 (569)	31 (217)	26 (179)
RP-2	12	2	1144 (618)	29 (203)	30 (207)
RP-1	19	2	1074 (579)	26 (180)	30 (210)
RP-2	11	2	1085 (585)	30 (205)	33 (225)
RP-TS-5	14	2	1130 (610)	32 (222)	35 (242)
JP-900	16	2	1015 (546)	31 (217)	45 (313)
JP-7	15	2	950 (510)	30 (205)	50 (343)
RP-1	8	2	964 (518)	35 (241)	79 (545)
RP-1	5	2	985 (529)	41 (281)	82 (563)
RP-1	2	7	1027 (553)	45 (311)	91 (625)
RP-1	17	1	964 (518)	31 (217)	103 (713)
RP-1	18	2	1005 (541)	30 (210)	188 (1293)

carbon (0 - ~230s); typically, small amounts of amorphous carbon (~230 - ~520s) and negligible filamentous carbon (~520 - ~800s) are present, with the exception of RP-1 (Sample 18), which deposited significantly more chemisorbed carbon than other fuels as well as measurable amorphous and filamentous carbon. The excessive levels of carbon formed from this fuel correlate with its unusually large pressure drop increase (see Table 5). In contrast, UL-RP-1 (Sample 13) produced low amounts of chemisorbed carbon deposit in the heated region but significant filamentous carbon. This difference may help explain why the ΔP increase for this fuel was small (cf. Table 5) despite the relatively large amount of deposit formed: although additional testing is required for verification, filamentous carbon deposited in the heated region does not appear to adversely impact channel fluid dynamics at these geometrical and flow scales.

In the exit region, all fuels exhibited measurable amorphous carbon deposit. Whereas most fuels deposited more heavily in the exit region, there were exceptions, including RP-1 (18), UL-RP-1 (13), and RP-1 (2). Higher deposit in downstream unheated regions may be due to the precipitation of solids out of the fuel and subsequent migration to cooler surfaces. Indeed, it seems evident from Figure 11 that appreciable deposit may occur at locations downstream of the last section, given the measurable but decreasing values near the end of the exit sections.

Summarizing the CRAFTI metrology, which comprises thermal integrity evaluation and test section TPO analysis of carbon deposit, the combined approach was shown to produce results that are repeatable, with characteristic physical and chemical behavior observed for tests performed at the same nominal operating conditions over an extended time period. Furthermore, the approach results in a physicochemical environment that effectively discriminates between fuels of different thermal quality; this characteristic is imperative for a method envisioned as providing pass/fail determination.

function of test article section in Fig. 11, with inlet, heated, and exit regions indicated by color (cf. Fig. 7). Section 22 (E11) was analyzed with TPO but excluded due to the large amount of carbon present at this location as a result of the graphite ferrule used to connect the test article to facility plumbing. As with ΔP increase and surface temperature, total carbon results demonstrate the ability of the test to distinguish thermally stable fuels. It is striking to note that the seemingly tight fuel specification controls on fuel-bound sulfur, aromatic, and olefin compounds still allow order-of-magnitude differences in total deposit quantity.

Additional insight is gained by examining the type of carbon formed, information that is lost when integrating the TPO signal. Figure 12 presents TPO carbon of several fuels as a function of analysis time and temperature for the heated and exit regions. In the heated region, the greatest contributor is chemisorbed

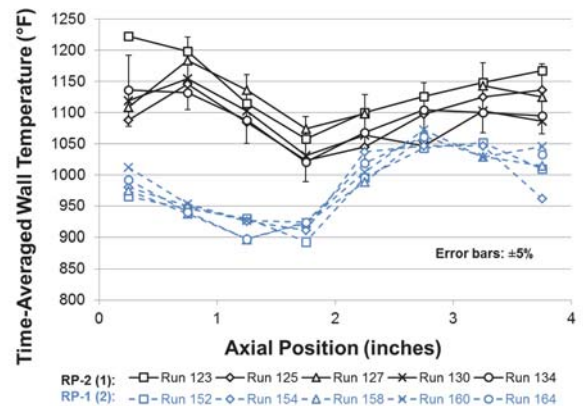


Figure 10. Heated region wall temperature is repeatable and sensitive to fuel composition

C. Principal Components Analysis (PCA)

Given the multitude of influencing parameters on the processes of fuel thermal decomposition and deposit formation, the development of rigorous correlations encompassing these multivariate data would appear out of reach. Indeed, considering only fuel compositional influences on surface fouling (i.e., quantity and type of sulfur-containing compounds, quantity and type of aromatic compounds, nitrogen-containing compounds, oxygenated compounds, unsaturated aliphatic compounds, etc.), the task seems daunting. However, the research team has made progress in previous efforts of a similar nature, and attempted for the AFQTMoDev project to follow a similar course, namely, the application of a variety of chemometric tools to the problem of complex, multivariate datasets. Rather than an extensive presentation of the outcomes of chemometrics and model development, select examples are given to illustrate their utility for the problem at hand; the interrelated nature of their application has already been discussed.

Figure 13 shows the three-dimensional (section location \times analysis time \times carbon counts) TPO carbon deposit data for RP-1 (2), which deposited chemisorbed carbon (0 - ~230s) in the heated region (sections 4-11) and amorphous carbon (~230 - ~520s) in the exit region (sections 12-21). To facilitate PCA implementation, TPO datasets for each fuel were created by averaging results from replicate runs. PCA was then performed on these datasets, resulting in a separation of the fuels into two different groups: fuels with large ΔP increase and those with small ΔP increase. This separation is indicated on PC 1 (30.79% captured variance) of the scores plot in Fig. 14. Although PCA was performed on TPO (not ΔP) data, PCA facilitates correlation between ΔP and carbon deposit, as indicated by the green and purple cluster boundaries shown (cf. Table 5, where fuels 2, 5, 8, 17, and 18 were the highest ΔP fuels tested).

Conspicuously absent from either cluster is RP-2 (Sample 13), which has been discussed previously as exhibiting abnormal deposit behavior and thereby atypical behavior based on carbon deposit.

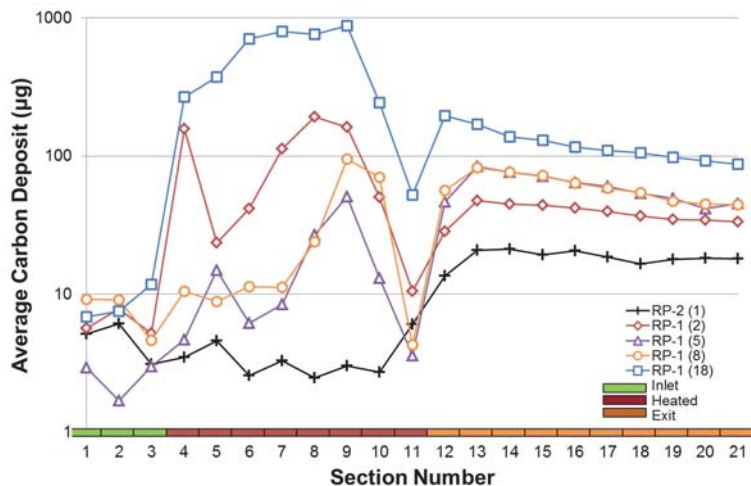


Figure 11. Total carbon deposit as a function of test article location demonstrates sensitivity to fuel composition

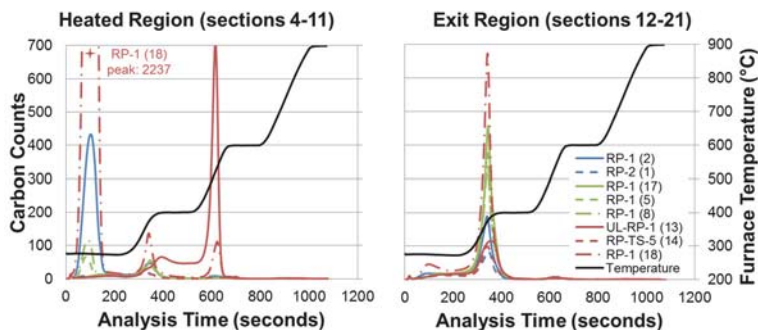


Figure 12. Carbon deposit in heated and exit regions varies with fuel composition. Approximate analysis times for deposits: chemisorbed: 0 - 230s; amorphous: 230 - 520s; filamentous: 520 - 800s; graphitic: >800s.

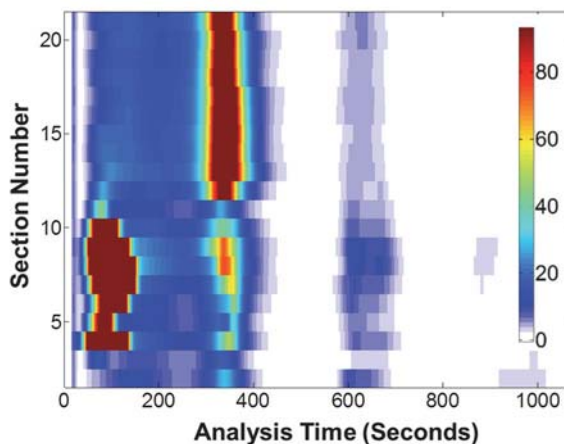


Figure 13. Representation of TPO carbon deposit for PCA. Fuel is RP-1 (Sample 2). Arbitrary legend units (normalized average of carbon counts).

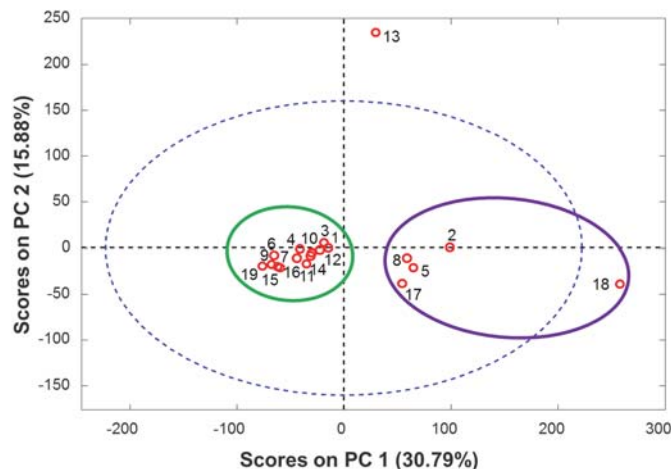


Figure 14. PCA scores plot for total carbon deposit. Data points represent fuel samples. High and low ΔP fuels indicated by purple and green boundaries.

PCA loadings plots are useful for identifying spatial and temporal variations in the TPO dataset (i.e., form of carbon) responsible for the separation observed in the scores plot. As presented here, positive contributions are indicated in blue and negative contributions are indicated in red. As shown in the loadings plot of Fig. 15, fuels are separated on PC 1 based on the amount of amorphous carbon deposit they produce (~230 - ~520s) in the heated and exit regions, given the highly positive contribution for sections 12-21 in particular. Therefore, the PC 1 clustering on the scores plot and the PC 1 loadings corroborate the assertion that amorphous carbon deposit in unheated exit sections is primarily responsible for increase in ΔP , although further examination of the peculiarity of RP-2 (13) and its large filamentous carbon deposit is required. Although not shown here, the loadings plot for PC 2 indicates strong positive contribution related to filamentous carbon (~520 - ~800s) in the heated region, consistent with the separation between RP-2 (13) and other fuels on the scores plot of Fig. 14.

In addition to TPO data, PCA was performed on ΔP , wall temperature, and comprehensive GC \times GC – TOFMS data. (For reference, Fig. 16 shows some representative chromatograms with general hydrocarbon regions identified.) In many cases, independent fuel data such as aromatic content served to establish apparent and perceived relationships. In general, the purpose of PCA was to define groups (or classes, although the term groups is used to avoid confusion with hydrocarbon classes) representative of high and low performing fuels.

D. Fisher Ratio Analysis

Following PCA, F-ratio analysis was implemented primarily to identify distinguishing chemical compounds that contribute to a fuel's group assignment. F-ratio analysis was performed using chromatographic features of five high performing fuels (6, 7, 9, 10, and 14) and five low performing fuels (2, 5, 8, 17, and 18), where general volatility behavior between the low and high performing fuels was relatively consistent to ensure that F-ratio analysis found

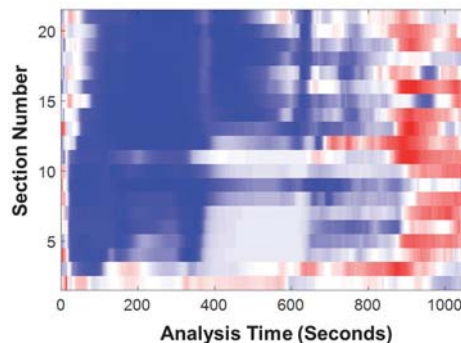


Figure 15. PC1 loadings plot for total carbon deposit. Positive and negative contributions on PC 1 are indicated by blue and red regions, respectively. ΔP increase is associated primarily with amorphous carbon in exit region (cf. Fig. 13 and 14).

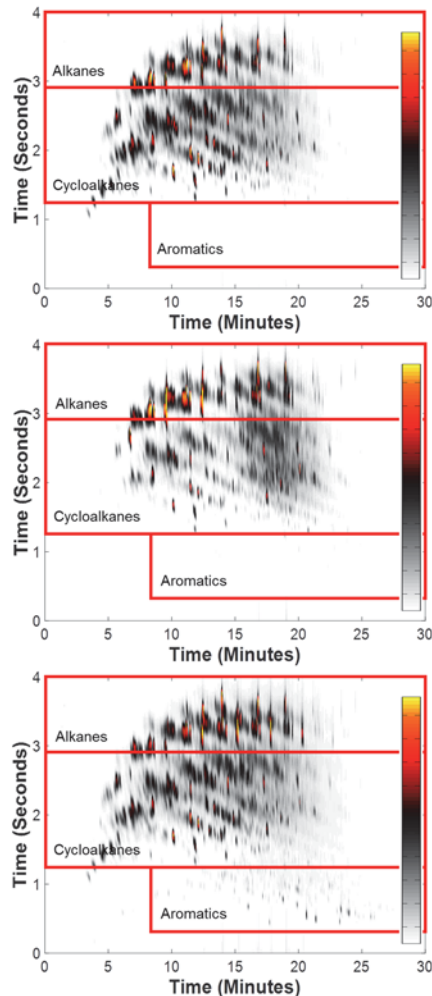


Figure 16. GC \times GC – TOFMS chromatograms for several representative fuels. Top: RP-2 (1); Middle: RP-2 (4); Bottom: RP-1 (2).

compounds related to thermal integrity while avoiding erroneous hits related to volatility differences. Tile-based F-ratio analysis can be used to tabulate compounds based on the ratio of between-group variance to within-group variance: Table 6 presents the top twenty F-ratio hits based on the training sets used [1st and 2nd dimension column retention time, match strength of compound identification, and the ratio of concentration in the low performing fuels to that in the high performing fuels (C-ratio) are also indicated]. Tiles (chromatographic compound locations)

Table 6. F-Ratio Analysis: Top Twenty Hits

#	F-Ratio	t_r^1 (min.)	t_r^2 (sec)	Compound	Match Value	C-ratio
1	277.1	18.7	0.91	1,1,6-trimethyltetralin	908	13.0
2	254.1	18.3	0.97	5-ethyltetralin	846	15.9
3	233.0	18.7	1.01	(1,4-dimethylpent-2-enyl)benzene	769	16.9
4	231.4	18.8	0.96	1-methyltetralin	751	6.3
5	219.4	16.5	1.20	(1-ethylbutyl) benzene	790	14.5
6	214.0	15.6	1.31	5-methylnonane	840	1.7
7	201.3	18.1	1.31	1,3,5-trimethyl-2-propylbenzene	894	11.9
8	188.5	23.6	0.64	2,6-dimethyl naphthalene	935	68.3
9	188.2	18.2	3.31	2,6-dimethyl heptadecane	900	5.0
10	182.9	17.3	1.43	adamantane	885	2.4
11	179.4	17.6	1.29	1-ethyl-2,4,5-trimethylbenzene	792	16.0
12	177.6	23.5	0.41	biphenyl	926	34.8
13	175.9	18.5	1.31	6-propyltetralin	735	9.1
14	172.4	18.9	0.81	6-methyltetralin	955	16.4
15	171.4	19.1	0.91	2,3-dimethyltetralin	711	4.6
16	169.0	17.5	1.31	1,4-dimethyl-2-(2-methylpropyl)-benzene	825	13.3
17	167.9	18.8	1.13	1-heptenylbenzene	794	10.1
18	164.6	17.7	1.19	(5-methyl-1-hexenyl)benzene	764	13.8
19	162.7	18.8	1.33	(1-methylhexyl) benzene	818	18.4
20	161.9	15.4	1.25	p-cymene	814	6.9

for the top 300 F-ratio hits are shown in Fig. 17. Although the appearance of aromatic compounds in Table 6 and Fig. 17 is not altogether surprising given their expected contribution to poor thermal stability, the results shown demonstrate the validity of the approaches used. It should be noted that F-ratio analysis does not indicate direct influences on thermal stability per se, but rather those compounds most responsible for the variance between two groups of fuels with different behavior. Ongoing work in this area includes obtaining more compositionally diverse fuels for inclusion in the training sets. Additionally, since F-ratio analysis is variance-based, compositional features that are indisputably related to poor thermal stability but may be found in only one or two of the low performing fuels may be overlooked (large within-group variance); to mitigate this, analyzing fuels with common but varied concentration of these compounds is underway.

E. Partial Least Squares (PLS) Modeling

Extensive PLS modeling was performed to relate chemical information contained in the GC×GC – TOFMS data to CRAFTI behavior and TPO carbon deposit characteristics. PLS results shown here were obtained using leave-one-out-cross-validation (LOOCV), a process that generates N different models, each of which is generated using N – 1 datasets consisting of GC×GC – TOFMS and measured performance behavior. With LOOCV, each of the N models is constructed while “leaving out” data for a single fuel in the set, resulting in a prediction based on N – 1 datasets. This model is then used to predict the performance behavior (maximum pressure drop, carbon deposit, etc.) of the fuel that was left out. This process is performed N times (once for each fuel), and the resulting predictions are compared graphically and statistically with the corresponding measured values. Root mean squared error of

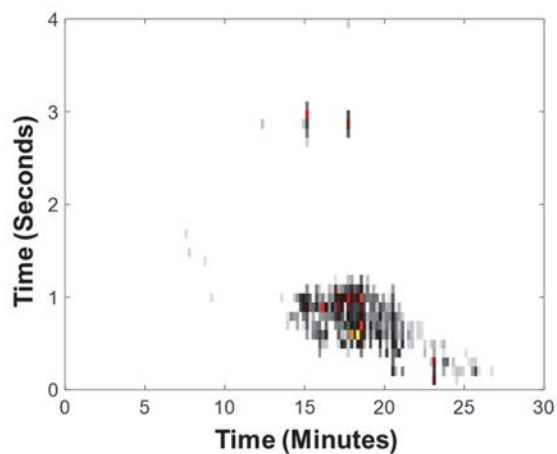


Figure 17. Chromatographic tile locations for top 300 F-ratio hits. Color scale corresponds to F-ratio (largest to smallest): red, orange, yellow, black, gray shades.

cross validation (RMSECV) and normalized root mean squared error of cross validation (NRMSECV) were used to assess predictive quality of models:

$$\text{RMSECV} = \left[\left(\frac{1}{N} \right) \times \sum (y_{i,cv} - y_{i,meas})^2 \right]^{0.5} \quad (1)$$

$$\text{NRMSECV} = \left(\frac{\text{RMSECV}}{|y_{max,meas} - y_{min,meas}|} \right) \times 100 \quad (2)$$

In these definitions, N is the number of samples, y is the numerical value of the property or metric being evaluated, and the subscripts i , cv , $meas$, max , and min denote sample index, modeled value, measured value, maximum value, and minimum value, respectively.

As with PCA, PLS modeling was performed for several experimentally measured variables. Figure 18 presents the results of PLS modeling (using only the top 300 F-ratio chromatographic locations) of a conveniently simple yet descriptive parameter defined to describe fuel thermal integrity, referred to as Thermal Integrity Index (TII):

$$\text{TII} \propto \frac{1}{\Delta P \times C_{A,exit}} \quad (3)$$

ΔP in this relation is the maximum pressure drop, which typically occurred near the end of each test. The other term in the denominator is simply the average amorphous carbon signal obtained for the exit region sections. Scaling was performed to obtain TII values between 0 and 100.

With NRMSECV of 16.7%, this model has room for improvement, such as the inclusion of low concentration (<100 ppm) compounds contributing to thermal stability, varying fuel thermophysical properties and their temperature dependence, and most importantly an extended set of fuels for the model training set. Nonetheless, the uncertainty in measured values must also be considered when judging the quality of the model (cf. Figure 8). Furthermore, considering the general compositional similarity for many of the specialty commodity samples procured for this effort, the definition of TII and its predictability using only GC×GC – TOFMS data is encouraging at this stage in the project. These results represent the first time that specialty aerospace fuels have been systematically assessed in a representative thermal quality test and simultaneously analyzed with advanced chromatographic techniques, for the ultimate purpose of predictive model development leading to intentional fuel formulation.

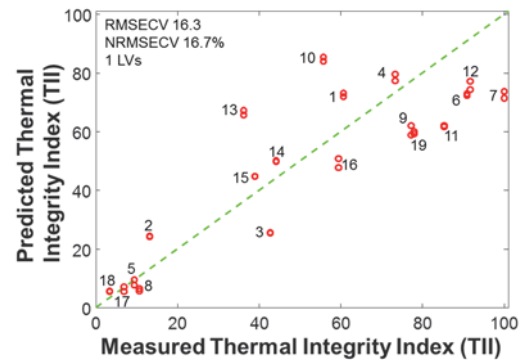


Figure 18. PLS model of thermal integrity index (TII). Predicted value for each fuel based on GC×GC – TOFMS data. Green dashed line (1:1) indicates perfect agreement.

IV. Conclusions

A compact apparatus to rapidly assess fuel thermal integrity was developed and applied to a set of rocket kerosene fuels. Its viability as a reliable test metrology was evaluated by demonstrating that it: (1) possesses qualities characteristic of a standard test method, such as automation, ease of assembly, safe operation, etc.; (2) produces meaningful data in a short timeframe with small fuel quantities; (3) operates at conditions relevant to the intended application; (4) acquires thermal performance data with good repeatability; and (5) discriminates between fuels that are otherwise indistinguishable in terms of thermal integrity. Analysis of test data reveals that existing specification controls do not adequately ensure fuel thermal stability. This may be due in part to lack of precision and specificity for existing compositional limits, but more importantly underlines the need for a fuel thermal quality test.

Chemometric data analysis was applied to experimental and comprehensive GC×GC – TOFMS datasets, resulting in predictive models capable of correlating fuel composition with thermal integrity behavior such as pressure drop and carbon deposit. Data analysis tools (PCA, F-ratio, and PLS) were utilized to categorize fuels based on thermal performance, identify primary compositional differences between low performing and high performing fuels, and generate accurate predictive models that are amenable to datasets accompanying the multifaceted fuel thermal decomposition and deposit formation process. Results confirm the contribution of numerous chemical influences on thermal performance; these must be accounted for in the development of models that correlate fuel composition with fit-for-purpose quality.

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Certain commercial equipment, instruments, and materials are identified in this report to adequately specify the experimental apparatus and analytical approach. Such identification does not imply recommendation or endorsement by the United States Air Force, the Defense Logistics Agency, the Johns Hopkins University, and the University of Washington, nor does it imply that the equipment, instruments, and materials are the best available for the purpose.

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